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(54) Adhesive containing a polyurethane resin and process for producing a laminate

Klebstoff enthaltend ein Polyurethanharz und Verfahren zur Herstellung eines Laminats

Substance adhésive renfermant d'une résine polyuréthane et procédé de préparation d'agglomérés laminés

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Description

[0001] This invention relates to polyurethane resins, a process for producing the same and uses thereof. More particularly, the invention relates to water-based adhesive agents for film lamination and a method of making laminates using said adhesives.

[0002] With the increasing use of versatile flexible packagings, there has arisen a need to provide high performance printing inks, various coating agents, and adhesives that are applied for decorative, surface protecting, or other purposes.

[0003] Particularly in the food packaging industry, laminated flexible packagings are currently used since direct contact of the contents with inks must be avoided to ensure utmost hygiene while impressing consumers with the high quality of printing. Lamination is carried out by the two methods described hereunder: extrusion lamination which comprises printing an ink on various plastic film bases, applying a primer coat on the printed surface as required, and then laminating a molten layer of polyolefin or the like; and adhesive lamination which comprises applying an adhesive to the printed surface, and then laminating a plastic film. Whichever method is adopted, inks to be used on the various kinds of plastic films to be laminated are required to adhere strongly not only to the base film but also to the film to be laminated.

[0004] One application of laminated flexible packagings that is growing today involves boiling or retorting in hot water so as to cook or sterilize the contents thereof; in this case, the flexible packagings must withstand boiling or retorting without suffering from delamination.

[0005] Since the various aspects of ink performance depend primarily upon the performance of binder resins, solvent-based laminating using polyurethane resins as binders have heretofore been used extensively; those inks exhibit not only strong adhesion to various kinds of films but also good adaptability for laminating.

[0006] In contrast with such solvent-based laminating inks, the demand for the use of water-based printing inks is also increasing today in consideration of various aspects including environmental problems, labor saving, occupational safety and food hygiene. However, water-based printing inks generally exhibit low adhesion to plastic films and the peel strength of laminates; further, their adaptability for boiling and retorting is unsatisfactory.

[0007] Under these circumstances, the applicant previously filed Japanese Patent Application No. 354568/1991, in which he proposed a water-based laminating printing ink for use as a binder in a water-based polyurethane resin containing a polycarbonate diol as a diol component and which was improved in adhesion to various plastic films and peel strength of laminates. Flexible packagings produced by using such water-based laminating inks can be used to make bags for packaging dry foods but it does not have sufficient adaptability for making bags that can withstand boiling or retorting.

[0008] The applicant also filed Japanese Patent Application No. 317425/1992, in which he proposed a method for improving the adhesion to various plastic films and the peel strength of laminates by using, as an ink binder resin, an acrylic copolymer that had functional groups capable of reaction with a hydrazine group or a hydrazide group introduced into the molecule, and hydrazine compounds as a crosslinking agent, said agent with those functional groups and carbonyl groups that developed on the film surface by subsequent surface treatment. However, there is no guarantee for the occurrence of positive crosslinking said agents with the binder resins and the film surface, and this has often caused nonuniformity in adhesion and the peel strength of laminates.

[0009] EP-A-0 148 392 relates to aqueous solutions or dispersions of polyisocyanate polyaddition products, a method for their production and their use as adhesives or for producing adhesives. The method comprises the chain extension of a prepolymer obtained by reacting polyisocyanates and polyhydroxy compounds using an amine or hydrazine chain extender.

[0010] EP-A-0 259 679 relates to an adhesive essentially comprised of an aqueous solution or dispersion of a polyurethane with chemically incorporated carboxylate and/or sulfonate groups. The polyurethane is based on diisocyanates, dihydroxy compounds and an amine or hydrazine chain extender.

[0011] An aspect of the present invention is to provide a water-based laminating adhesive for plastic films that uses a polyurethane resin having at least one HYD. group in the molecule and an epoxy resin.

[0012] Another aspect of the present invention is to provide a process for producing a laminated product using said water-based laminating adhesive.

[0013] The polyurethane resin used in the present invention has a number average molecular weight of 2,000 - 200,000 and is prepared by reacting an organic diisocyanate compound, a polymer diol compound, a chain extender and a terminator, wherein a chain extender and/or a terminator that has at least one hydrazine group or hydrazide group is used to incorporate at least one of the HYD. groups in the molecule of the polyurethane resin. In a preferred case, said polyurethane resin has a molecular structure that is represented by the following general formula (1);

$$T_1 - (UP_1 - E_1) - \cdots - (UP_{n+1} - E_{n+1}) - UP_{n+2} - T_2 \quad (1)$$

where

UP_1 - UP_{n+2} : that part of a urethane prepolymer which excludes a terminated isocyanate group, said prepolymer being prepared by reacting the organic diisocyanate compound with the polymer diol compound, provided that n is an integer of 0 - 18 and that UP_1 - UP_{n+2} may have the same or different structures;

E_1 - E_{n+1} : that part of the chain extender which excludes the functional groups having reacted with the isocyanate group, said chain extender having at least two functional groups capable of reaction with the isocyanate group, provided that n is an integer of 0 - 18 and that E_1 - E_{n+1} may have the same or different structures;

T_1, T_2 : that part of the terminator which excludes the functional groups having reacted with the isocyanate group, said terminator having at least one functional group capable of reaction with the isocyanate group, provided that T_1 and T_2 may have the same or different structures; and

\- : the bond that has been formed by reaction between the isocyanate group and the functional group capable of reaction with said isocyanate group:

provided that at least one of E_1 - E_{n+1}, T_1 and T_2 has at least one hydrazine group or hydrazide group.

[0014] The general formula (1) is a schematic presentation and shows only a straight-chained structure but it should be noted that the general formula (1) may partly contain a branched chain.

[0015] The polyurethane resins used in the present invention have at least one of the HYD. groups introduced into the molecule using a chain extender and/or a terminator that has at least one hydrazine group or hydrazide group; hence, the following description also covers such chain extender and terminator that have at least one hydrazine group or hydrazide group. Further, when one wants to use the polyurethane resins for water-based printing inks or water-based laminating adhesives, the resins are dispersed in water in the presence of an emulsifier or, alternatively, the polyurethane resins having free carboxyl groups are dissolved or dispersed in an aqueous alkali solution or, the polyurethane resins having tertiary amino groups are dissolved or dispersed in an aqueous acid solution. Hence, the following description also covers the polymer diol compound and chain extender containing a free carboxyl group or a tertiary amino group for introducing the free carboxyl group or tertiary amino group into the molecule of the polyurethane resins.

[0016] First, the organic diisocyanate compound is discussed. The organic diisocyanate compound is selected from the group consisting of aliphatic diisocyanate compounds such as hexamethylene diisocyanate and 2,2,4-trimethylhexamethylene diisocyanate, alicyclic diisocyanate compounds such as isophorone diisocyanate, hydrogenated xylylene diisocyanate and 4,4-cyclohexylmethane diisocyanate; aroaliphatic diisocyanate compounds such as xylylene diisocyanate and tetramethylxylylene diisocyanate, and aromatic diisocyanate compounds such as toluylene diisocyanate and diphenylmethane diisocyanate. Among these compounds alicyclic or aroaliphatic diisocyanate compounds are preferred since they provide good adhesion to various kinds of films and insure efficient redissolution of water-based printing inks.

[0017] The polymer diol compound is selected from the group consisting of polyester diols that are prepared by polycondensation of low-molecular weight diols (e.g., straight-chained glycols such as 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol, branched glycols such as 1,2-propanediol, neopentyl glycol, 3-methyl-1,5-pentanediol and ethylbutylpropanediol, and ether-base diols such as diethylene glycol and triethylene glycol) with dibasic acid compounds such as adipic acid and phthalic acid, or by the ring-opening reaction of cyclic ester compounds such as lactones; polyether diols that are prepared by homo- or copolymerizing ethylene oxide, propylene oxide, tetrahydrofuran; polycarbonate diols that are prepared by reacting carbonate compounds (e.g., alkylene carbonates, diallyl carbonates and dialkyl carbonates) or phosgene with the above-mentioned low-molecular weight diol components; and polybutadiene glycols.

[0018] Examples of the polymer diol compound having a free carboxyl group include those which are prepared by reacting the above-mentioned polymer diol components with tetrabasic acid anhydrides such as pyromellitic anhydride or by the ring-opening polymerization of lactones in the presence of dimethylolpropionic acid or other initiators.

[0019] Examples of the polymer diol compound having a tertiary amino group include those which are prepared by the ring-opening polymerization of alkylene oxides, lactones, etc. in the presence of an initiator selected from among amino containing diol compounds such as N-methyldiethanolamine.

[0020] The polymer diol compounds that can preferably be used have molecular weights in the range from 500 to 4000.

[0021] If one wants to use the polyurethane resins as binders in printing inks and the like, from the view of obtaining a resin which has good adhesion to plastic film and high adaptability for making laminates, polyester diols and polycarbonate diols can preferable be used. If adaptability for boiling and retorting is necessary , polyester diols may be used with advantage.

[0022] We next discuss the chain extender that is used for extending the chains of the urethane prepolymer.

[0023] This chain extender is selected from the group consisting of polyamino hydrazine compounds that are repre-

sented by the general formula (2) discussed below; compounds having a tertiary amino group; carboxylic acid compounds represented by the general formula (3) discussed below; diols containing an aliphatic carboxylic acid group and being formed by reacting succinic anhydride or maleic anhydride with lower triols; diols containing aromatic carboxylic acid groups and being formed by reacting phthalic anhydride or trimellitic anhydride with lower triols or pyromellitic anhydride with lower diols; glycols; aliphatic diamines; aliphatic polyols; alicyclic polyols; and aliphatic polyamines.

[0024] The chain extender represented by the following general formula (2) is a polyamino hydrazine compound:

$$H_2N - R_1 - NH - CH_2 - \underset{\displaystyle R_2}{\underset{|}{CH}} - \underset{\displaystyle O}{\underset{\|}{C}} - NH - NH_2 \quad \cdots (2)$$

where R_1 is an alkylene group having 2 to 15 carbon atoms, that portion of an alicyclic or aromatic diamine having 6 - 15 carbon atoms which excludes the amino group, or that portion of a polyethylene polyamine having 3 to 5 nitrogen atoms which excludes the primary amino group; and R_2 is hydrogen or a methyl group.

[0025] The chain extender of the general formula (2) can be prepared in accordance with a known method (as described in Japanese Patent Publication No. 8649/1991) that starts with forming a Michael addition compound between a polyamine and a (meth)acrylic acid derivative and which then involves an ester exchange between hydrazine and the (meth)acrylic acid ester portion.

[0026] Examples of the polyamine that can be used in the synthesis of the polyaminohydrazide include aliphatic diamines having 2 - 15 carbon atoms such as ethylenediamine, butylenediamine, hexamethylenediamine and trimethylhexamethylenediamine, alicyclic or aromatic diamines having 6 - 15 carbon atoms such as diaminobenzene, xylylenediamine, 4,4'-diaminobicyclomethane, 1,4-diaminocyclohexane, 1,4-bis(aminomethyl)cyclohexane and isophoronediamine, as well as diethylenetriamine, triethylenetetramine and tetraethylene-pentamine.

[0027] Exemplary (meth)acrylic acid derivatives include alkyl esters, hydroxyalkyl esters and aminoalkyl esters of acrylic or methacrylic acid. Among these compounds, acrylic acid derivatives are preferred in view of their high reactivity.

[0028] Exemplary chain extenders having a tertiary amino group include N-alkyldialkanolamine compounds such as N-methyldiethanolamine and N-ethyldiethanolamine, and N-alkyldiaminoalkylamine compounds such as N-methyldiaminoethylamine and N-ethyldiaminoethylamine.

[0029] A chain extender having a free carboxyl group may be used to produce water-based polyurethane resins. Such chain extenders are compounds represented by the following general formula (3)

$$HO - CH_2 - \underset{\displaystyle COOH}{\underset{|}{\overset{\displaystyle R_3}{\overset{|}{C}}}} - CH_2 - OH \quad \cdots (3)$$

where R_3 is a hydrogen atom or a straight-chained or branched alkyl group having 1 to 8 carbon atoms; diols containing an aliphatic carboxylic acid group and being formed by reacting succinic anhydride or maleic anhydride with lower triols; or diols containing aromatic carboxylic acid groups and being formed by reacting phthalic anhydride or trimellitic anhydride with lower triols or pyromellitic anhydride with lower diols.

[0030] To the group of compounds from which the chain extender is selected belong, in addition to the compounds mentioned above, glycols such as ethylene glycol and propylene glycol, aliphatic diamines such as ethylenediamine, 1,4-butanediamine and aminoethylethanolamine, aliphatic polyols such as glycerin, 1,2,3-trimethylolpropane and pentaerythritol, alicyclic polyols such as 1,3,5-cyclohexanetriol, and aliphatic polyamines such as diethylenetriamine, triethylenetetramine and tetraethylenepentamine.

[0031] If compounds having at least three functional groups capable of reaction with the isocyanate group are used as chain extenders, branches may occasionally form in the molecule of polyurethane.

[0032] We next discuss the terminator.

[0033] After the urethane prepolymer has been extended with the chain extender, the reaction is terminated with terminator.

[0034] The terminator is selected from the group consisting of the compounds listed above as chain extenders, hydra-

zine, alkylene dihydrazines, alkylene dihydrazides, and dihydrazide compounds of saturated aliphatic dibasic acids or unsaturated dibasic acids that are represented by the following general formula (4):

$$H_2N - NH - X - NH - NH_2 \qquad (4)$$

where X is an alkylene group having 1 to 8 carbon atoms or a carbonyl residue of a saturated or unsaturated dibasic acid having 1 to 10 carbon atoms; alkyl amines; alkanol amines; and monoalcohols.

[0035] Specific examples of the alkylenedihydrazine include methylenedihydrazine, ethylenedihydrazine, propylenedihydrazine and butylenedihydrazine. Specific examples of the dihydrazide compound of a saturated aliphatic dibasic acid include oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide and sebacic acid dihydrazide. Specific examples of the dihydrazide compound of an unsaturated dibasic acid include phthalic acid dihydrazide, fumaric acid dihydrazide and itaconic acid dihydrazide.

[0036] Other useful terminator include alkylamines such as n-propylamine, n-butylamine and N,N-di-n-butylamine, alkanolamines such as monoethanolamine and diethanolamine, and monoalcohols such as methanol and ethanol. The chain extenders described before may also be used as the terminator.

[0037] The above-described organic diisocyanate compound, polymer diol compound, chain extender and the terminator are used to produce the polyurethane resin by the following procedure.

[0038] The process starts with reacting the organic diisocyanate compound with the polymer diol compound at a molar ratio (diisocyanate/polymer diol) of (1.3/1.0 - 3.0/1.0), preferably (1.5/1.0 - 2.0/1.0) to synthesize a urethane prepolymer. Then, the chain extender is added in an amount 0.5 - 0.95 times the equivalent amount of the residual isocyanate group, optionally in the presence of a solvent, a catalyst and the like, and reaction is carried out at a temperature of 30 - 140°C; thereafter, the reaction of the residual isocyanate groups is stopped with the terminator to complete the process of production of the polyurethane resin.

[0039] The polyurethane resin produced by this method is characterized in that individual molecules are substantially uniform in structure; in addition, the molecular distribution of the polyurethane resin are so narrow that it is preferably used as a binder resin for inks or as an adhesive.

[0040] The polyurethane resin can also be produced by feeding in the same batch the organic diisocyanate compound, polymer diol compound, chain extender, terminator and, optionally, a catalyst and a solvent. However, in this case, it is difficult to control the molecular structures of the polyurethane resin and its molecular weight and with this resin, one cannot ensure the same performance; hence, the use of the product polyurethane resin is limited.

[0041] The polyurethane resins that are produced from the materials described above by the method that is also described above have molecular weights of 2,000 - 200,000, preferably from 10,000 to 100,000. If the molecular weight of the polyurethane resins is less than 2,000, the resin's film lacks elasticity and toughness If the molecular weight of the polyurethane resins exceeds 200,000, the water-based polyurethane resins as dissolved in the aqueous alkali or acid solution to be described hereinafter will become highly viscous; in the case of the water-based polyurethane resins as dispersed in the aqueous alkali or acid solution or in water in the presence of an emulsifier, the dispersion stability will decrease.

[0042] In the process of reaction involving the polyurethane resin, it cannot be said that the chain extender or terminator that have at least one hydrazine group or hydrazide group are distributed uniformly in all molecules of the polyurethane resin: however, the performance required by the present invention is achieved if the polyurethane resin has at least one of the HYD. groups on average per molecule.

[0043] We next describe the methods to dissolve or disperse the polyurethane resin in water. The first method to be adopted comprises dispersing the polyurethane resin in water in the presence of an emulsifier. This method can be implemented by two approaches; in one approach, the urethane prepolymer prepared by reacting the organic diisocyanate compound with the polymer diol compound is dispersed in water in the presence of an emulsifier and then extended with the chain extender, and the reaction is terminated by means of the terminator. In the other approach, the urethane prepolymer is dissolved in a water-miscible solvent such as acetone or methyl acetate, and chains in the prepolymer are extended with the chain extender, and the reaction is terminated by means of the terminator; thereafter, the reaction product is mixed with water containing an emulsifier, and the solvent is distilled off.

[0044] Examples of the emulsifier that can be used in this method include anionic surfactants such as higher alcohol sulfate ester salts, alkylbenzenesulfonate salts and polyoxyethylene alkyl sulfate ester salts, and nonionic surfactants such as polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenylethers and sorbitan derivatives. These emulsifiers can be used either alone or in admixtures.

[0045] By this method, the polyurethane resin can be dispersed in water irrespective of whether the molecule of the polyurethane resin contains or does not contain a carboxyl group or a tertiary amino group.

[0046] The second method to be adopted for rendering the polyurethane resin to be water-based comprises dissolving or dispersing said resin in an aqueous alkali solution. To implement this method, a polymer diol compound or chain extender that have a free carboxyl group must be used.

[0047] The polyurethane resin must have an acid value of more than 5 to be dissolved or dispersed in an aqueous alkali solution. If the acid value of the polyurethane resin is less than 5, it is difficult for the resulting water-based polyurethane resin to maintain a stable dispersed state by itself in the water-based system. If the acid value of the polyurethane resin exceeds 100, the formed film will become too hard to provide satisfactory physical properties. Hence, the content of the carboxyl group in the polymer diol compound or chain extender must be properly adjusted in accordance with the specific use of the polyurethane resin and the required performance.

[0048] Alkali compounds that are to be used in aqueous solution include ammonia, organic amines and alkali metal hydroxides. Specific examples of organic amines include alkylamines such as diethylamine, triethylamine and ethylenediamine, and alkanolamines such as monoethanolamine, ethylethanolamine and diethylethanolamine. Specific examples of alkali metal hydroxides include sodium hydroxide and potassium hydroxide.

[0049] The third method to obtain the water-based polyurethane resin comprises dissolving or dispersing the resin in an aqueous acid solution. To implement this method, a polymer diol compound and/or chain extender that have a tertiary amino group must be used.

[0050] The polyurethane resin must have an amine value of more than 10 to be dissolved or dispersed in an aqueous acid solution. If the amine value of the polyurethane resin is less than 10, it is difficult for the resulting water-based polyurethane resin to maintain a stable dispersed state in the water-based system. If the amine value of the polyurethane resin exceeds 40, the resin's film that is formed will become too hard to provide satisfactory physical properties. Hence, the content of the tertiary amino group in the polymer diol compound or chain extender oust be properly adjusted in accordance with the specific use of the polyurethane resin and the required performance.

[0051] Acids that are to be used in aqueous solution include inorganic and organic acids such as hydrochloric acid, nitric acid and acetic acid.

[0052] The solids content of the water-based polyurethane resins, described hereinabove is advantageously in the range from 5 to 50 wt%. If the solids content of the water-based polyurethane resin is less than 5 wt%, the concentration of the resin is so low that its use is limited. If the solids content of the water-based polyurethane resin exceeds 50 wt%, it is difficult for the resin to be efficiently dissolved or dispersed in water.

[0053] The alkali or acid to dissolve or disperse the polyurethane resin in water is used in an amount 0.15 - 1.2 times the equivalent amount (neutralization rate = 100%) which is necessary to neutralize the polyurethane resin. If the use of the alkali or acid is less than 0.15 times the equivalent amount, it becomes difficult for the polyurethane resin to be effectively dispersed in water. If desired, the alkali or acid may be used in excess of 1.2 times the equivalent amount; however, the effectiveness of the alkali or acid to dissolve or disperse the polyurethane resin in water will not differ greatly from the case where they are used in an amount 1.2 times the equivalent amount.

[0054] We next describe the uses of the polyurethane resin. First, the water-based polyurethane resin can be used as a binder for water-based printing ink compositions. The water-based printing ink composition comprises a pigment, a water-based binder resin, water and a water-miscible solvent as an optional component and this ink composition is intended for use on plastic films.

[0055] The pigment may be selected from among inorganic pigments, organic pigments and fillers that are commonly used in printing inks, paints and the like. The pigment is advantageously used in amounts ranging from 5 to 60 wt% of the ink composition.

[0056] The water-based binder resin contains as the essential component the water-based polyurethane resin which is specified herein: this water-based polyurethane resin may be dispersed in water in the presence of an emulsifier or it may be dissolved or dispersed in an aqueous alkali or acid solution, and either type or water-based binder resin may be used.

[0057] The water-based printing ink composition may contain an epoxy resin as a crosslinking component and this contributes to the manufacture of laminated products that have better adaptability for boiling or retorting.

[0058] Examples of the useful epoxy resin include the bisphenol-epichlorohydrin epoxy resin, cycloaliphatic epoxy resins, novolak epoxy resins, epoxy olefinic resins, polyolglycidyl epoxy resins, epoxidized soybean oil and silane epoxy resins.

[0059] Among these epoxy resins, those which will not dissolve or disperse in water on their own may be added after being forcibly emulsified in water with the aid of an emulsifier.

[0060] From the viewpoint of reactivity with the epoxy resin, it is more preferable to use a polyurethane resin that is specified herein and which also contains in the molecule a carboxyl group that is directly bonded to the aromatic ring.

[0061] In the case under consideration, the polyurethane resin which is specified herein and the epoxy resin are mixed typically at a weight ratio of 99:1 - 50:50 (polyurethane resin : epoxy resin), preferably at a weight ratio in the range from 95:5 to 60:40.

[0062] With a view to improving other aspects of the ink performance, various other water-based resins may be added as exemplified by cellulosic resins, acrylic resins, polyester resins, styrene-maleic acid based resins, ethylene-acrylic acid based resins, and polyurethane resins that do not have HYD. groups in the molecule.

[0063] These water-based binder resins are preferably used in such amounts that the solids content of the resin is in

the range from 5 to 30 wt% of the ink composition.

[0064] Depending upon the need for other aspects of ink performance, it is possible to incorporate water-miscible solvents such as lower alcohols or alkoxypropanols (e.g., methanol, ethanol, isopropanol and methoxypropanol), as well as various additives including anti-blocking agents, defoamers and crosslinking agents other than epoxy resins.

[0065] Using the materials listed above, one can produce a water-based printing ink composition by a process that comprises first mixing a pigment with the water-based binder resin under agitation, then blending the ingredients of the mixture in a conventional disperser, further adding predetermined components, and finally mixing all ingredients to homogeneity.

[0066] Another use of the water-based polyurethane resin is as a water-based laminating adhesive. For imparting better adaptability for boiling and retorting, the water-based polyurethane resin is used in combination with an epoxy resin that is selected from among the epoxy resins that have been listed hereinabove as crosslinking components of the water-based printing ink composition. From the viewpoint of reactivity with epoxy resins, the polyurethane resin specified herein may preferably be selected from among those which have in the molecule a carboxyl group that is directly bonded to the aromatic ring.

[0067] In the case under consideration, the water-based polyurethane resin specified herein is mixed with the epoxy resin at a weight ratio that typically ranges from 99:1 to 50:5,0 (polyurethane resin : epoxy resin), preferably from 95:5 to 60:40. If the mixing ratio of the epoxy resin exceeds 50:50, adhesive strength will drop to an undesirably low level.

[0068] We next describe the method of lamination using the water-based ink composition and/or water-based laminating adhesive according to the present invention. The water-based ink composition can be printed on various kinds of plastic films such as polyolefin, modified polyolefin, polyester, nylon and polystyrene films. It is particularly preferable to print on plastic films that have been subjected to corona discharge treatment or surface coating treatments. The water-based ink composition can be printed by flexographic or gravure printing techniques with known flexographic or gravure presses.

[0069] The printed matter thus produced may be worked into laminates by either extrusion laminating or adhesive laminating processes. When applying the extrusion laminating process, the water-based laminating adhesive of the present invention or any one of the conventionally used primer coat including titanium, isocyanate, imine and polybutadiene base compounds is applied to the surface of the printed matter and a molten polymer is laminated by means of a known extrusion laminating machine: if desired, the molten resin may be overlaid with another material (ex. aluminum foil), thus producing a sandwich structure in which the molten resin forms an intermediate layer.

[0070] The resin to be melted in the extrusion laminating process may be selected from among conventionally used resins such as low-density polyethylene, ethylene-vinyl acetate copolymer and polypropylene. Among these resins, the low density polyethylene which is oxidized upon melting to increase the change of the generation of carbonyl groups is preferred since the advantages of the present invention are attained with higher efficiency.

[0071] When applying the adhesive laminating process, the water-based laminating adhesive of the present invention is applied to the surface of the printed matter and a polymer film is bonded by means of a known adhesive laminating machine.

[0072] The polymer film to be used in the adhesive laminating process may be selected from the films of polyethylene, polypropylene, etc. Particularly in the case of making laminates that are to be retorted, hot water resistance may be imparted by sandwiching an aluminum foil between the base and the plastic film.

[0073] In order to produce laminates using a completely water-based ink and adhesive so that there will be no problems in safety, hygiene and environmental aspects, the water-based ink is preferably used in combination with a water-based or solvent-free adhesive.

[0074] The laminates produced by the methods described above have not only high strength but also good adaptability for boiling and retorting. If the water-based printing ink composition and water-based laminating adhesive of the present invention are used in combination, laminates can be produced that have the added advantage of assuring safety, hygiene and environment friendliness.

[0075] The water-based polyurethane resin that is specified herein and which has at least one HYD. groups in the molecule exhibit strong adhesion to various kinds of plastic films and it is particularly useful on plastic films that have been subjected to corona discharge and other treatments to have keto groups formed on the surface. This would be explained as follows: only a weak interaction (ex. chemical adsorption) works between the conventional polyurethane resin and the surface of a plastic film; in contrast, a very strong bonding force due to the dehydrative condensation reaction between the HYD. groups and the keto group works between the polyurethane resin and the surface of a plastic film.

[0076] The polyethylene to be used in the extrusion laminating process is oxidized with oxygen in air to generate keto groups in the molecule while it is thermally melted and laminated on the printed surface: thus, for the same reason as stated above in connection with surface treated polymer films, laminates having very high strength can be produced.

[0077] Hence, despite its water-based nature, the printing ink that uses the polyurethane resin exhibits good adhesion to various kinds of plastic films and enables the production of very strong laminates.

[0078] The polyurethane resin does not have any functional groups in the molecule that will react with HYD. groups and, hence, neither intramolecular nor intermolecular crosslinking will occur, and this offers the advantage that the ink that uses the polyurethane resin as a binder can be stored for a prolonged time without experiencing any drop in fluidity and capability for redissolution.

[0079] If desired, an epoxy resin may be added as a crosslinking agent immediately before printing is done with the water-based ink composition; in this case, a crosslinking reaction occurs between the epoxy and polyurethane resins after printing, whereby a marked improvement is achieved in resistance to both heat and water, thus making it possible to produce laminates having good adaptability for boiling and retorting.

[0080] On the pages that follow, the present invention is described in greater detail with reference to working examples but it should be noted that those examples are by no means limiting. In the following synthesis examples, working examples and comparative examples, all "parts" and "percentages" are by weight unless otherwise noted.

Synthesis Example 1: Synthesis of a Polyaminohydrazide (Composition of Compound A)

[0081] A four-necked flask equipped with a stirrer, a condenser, a N_2 gas introducing tube and a dropping funnel was charged with 158.3 parts of trimethylhexamethylenediamine, which was heated at 45°C while N_2 gas was introduced; thereafter, 100 parts of ethyl acrylate that had been heated at 45 - 50°C was added dropwise over 90 min.

[0082] The resulting reaction product was warmed at 45°C for 7 h until the reaction was completed. Then, 50 parts of a hydrazine hydrate that had been heated at 50°C was added, followed by heating at 65°C to perform a reaction for 5 h until the composition of compound A was obtained.

Synthesis Example 2: Synthesis of an Aromatic Carboxylic Acid Containing Diol Compound (Solution of Compound B)

[0083] Equipment of the same construction as used in Synthesis Example 1 was charged with 148 parts of phthalic anhydride, 134 parts of trimethylolpropane and 300 parts of dried 2-methylpyrrolidone and the mixture was heated at 80°C to initiate a reaction, which was performed until the anhydride group disappeared, thus yielding a solution of compound B.

Synthesis Example 3

[0084] A four-necked flask equipped with a stirrer, a condenser and a N_2 gas introducing tube was charged with 300 parts of polybutylene glycol adipate diol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 2 h while N_2 was introduced. Subsequently, 24.1 parts of dimethylolpropionic acid was added and the reaction was continued at 80 - 90°C for 2 h. After confirming the completion of the reaction of dimethylolpropionic acid, 1137 parts of water and 21.2 parts of triethylamine were fed to make a water-based system; further, 28.1 parts of the composition of compound A was fed to perform chain extension, followed by feeding 3.7 parts of monoethanolamine to terminate the reaction, whereby solution sample No. 1 of a water-based polyurethane resin was obtained (acid value of this polyurethane resin: 20.9, neutralization rate: 100%).

Synthesis Example 4

[0085] Equipment of the same construction as used in Example 1 was charged with 300 parts of polybutylene glycol adipate diol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 4 h while N_2 gas was introduced. Subsequently, 34.2 parts of dimethylolpropionic acid was fed and the reaction was continued at 80 - 90°C for 2h.

[0086] After confirming the completion of the reaction of dimethylolpropionic acid, 1134 parts of water and 26 parts of triethylamine were fed to make a water-based system; further, 28 parts of the composition of compound A was fed to terminate the reaction, whereby solution sample No. 2 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 29.6, neutralization rate: 100%)

Synthesis Example 5

[0087] Equipment of the same construction as used in Example 1 was charged with 300 parts of polypropylene glycol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 6 h while N_2 gas was introduced. Subsequently, 30.4 parts of N-methyldiethanolamine was fed and the reaction was continued at 80 - 90°C for 3 h. After confirming the completion of the reaction of N-methyldiethanolamine, 1124 parts of water and 15 parts of acetic acid were fed to make a water-based system; further, 28 parts of the composition of compound A was fed to terminate the reaction, whereby solution sample No. 3 of a water-based

polyurethane resin was yielded. (amine value of this polyurethane resin: 31.9, neutralization rate: 100%)

Synthesis Example 6

[0088] Equipment of the same construction as used in Example 1 was charged with 300 parts of polybutylene glycol adipate diol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 4 h while N_2 gas was introduced. Subsequently, 24.1 part of dimethylolpropionic acid was fed and the reaction was continued at 100 - 110°C for 2 h.

[0089] After confirming the completion of the reaction of dimethylolpropionic acid, 943.7 parts of water and 16 parts of triethylamine were fed to make a water-based system; further, 12 parts of hydrazine hydrate was fed to terminate the reaction, whereby solution sample No. 4 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 22.2, neutralization rate: 100%)

Synthesis Example 7

[0090] Equipment of the same construction as used in Example 1 was charged with 300 parts of polybutylene glycol adipate diol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 4 h while N_2 gas was introduced. Subsequently, 92.0 parts of the solution of compound B was fed and the reaction was continued at 100 - 110°C for 2 h.

[0091] After confirming the completion of the reaction of compound B (aromatic carboxylic acid containing diol compound) in solution, 1121 parts of water and 16 parts of triethylamine were fed to make a water-based system; further 14.2 parts of hydrated hydrazine was fed to terminate the reaction, whereby solution sample No. 5 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 18.3, neutralization rate: 100%)

Synthesis Example 8

[0092] Equipment of the same construction as used in Example 1 was charged with 300 parts of a polyester diol (monomer unit: neopentyl adipate) having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 4 h while N_2 gas was introduced. Subsequently, 24.1 parts of dimethylolpropionic acid was fed and the reaction was continued at 100 - 110°C for 2 h.

[0093] After confirming the completion of the reaction of dimethylolpropionic acid, the reaction mixture was cooled to 100°C and 1002 parts of water and 31.9 parts of triethylamine were fed to make a water-based system; further 41.8 parts of adipic dihydrazide was fed to terminate the reaction, whereby solution sample No. 6 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 20.7, neutralization rate: 100%)

Synthesis Example 9

[0094] Equipment of the same construction as used in Example 1 was charged with 300 parts of a polycarbonate diol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyante, and a reaction was performed at 100 - 105°C for 4 h while N_2 gas was introduced. Subsequently, 24.1 parts of dimethylolpropionic acid was fed and the reaction was continued at 100 - 110°C for 2 h.

[0095] After confirming the completion of the reaction of dimethylolpropionic acid, 943.7 parts of water and 16 parts of triethylamine were fed to make a water-based system: further 12 parts of hydrated hydrazine was fed to terminate the reaction, whereby solution sample No. 7 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 22.2, neutralization rate: 100%)

Synthesis Example 10

[0096] Equipment of the same construction as used in Example 1 was charged with 300 parts of polypropylene glycol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 6 h while N_2 gas was introduced. Subsequently, 24.1 parts of dimethylolpropionic acid was added and the reaction was continued at 80 - 90°C for 2 h. After confirming the completion of the reaction of dimethylolpropionic acid, 1137 parts of water and 21.2 parts of triethylamine were fed to make a water-based system; further, 22.3 parts of the composition of compound A was fed to perform chain extension, followed by feeding 3.7 parts of monoethanolamine to terminate the reaction, whereby solution sample No. 8 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 21.3, neutralization rate: 100%)

Synthesis Example 11

[0097] Equipment of the same construction as used in Example 1 was charged with 300 parts of polybutylene glycol adipate diol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 4 h while N_2 gas was introduced. Subsequently, 148 parts of the solution of compound B was fed and the reaction was continued at 100 - 110°C for 2 h.

[0098] After confirming the completion of the reaction of compound B (aromatic carboxylic acid containing diol compound) in solution, the reaction mixture was cooled to 100°C and 1199 parts of water and 26 parts of triethylamine were added to make a water-based system; further, 22.2 parts of the composition of compound A was fed to terminate the reaction, whereby solution sample No. 9 of a water-based polyurethane resin was yielded. (acid value of this polyurethane: 27.1, neutralization rate: 100%)

Synthesis Example 12

[0099] Equipment of the same construction as used in Example 1 was charged with 300 parts of polybutylene glycol adipate diol having an average molecular weight of 1000 and 32.7 parts of pyromellitic anhydride, and a reaction was performed at 85 - 90°C for 2 h; thereafter, 53.3 parts of isophorone diisocyanate was added and the reaction was continued at 60 - 70°C for 4 h while N_2 gas was introduced.

[0100] Subsequently, 912 parts of water and 30.3 parts of triethylamine were added to make a water-based system; further, 3.3 parts of ethylenediamine and 3.6 parts of hydrazine hydrate were fed to terminate the reaction, whereby solution sample No. 10 of a water-based polyurethane resin was yielded (acid value of this polyurethane resin: 42.9, neutralization rate: 100%).

Synthesis Example 13

[0101] Equipment of the same construction as used in Example 1 was charged with 500 parts of polypropylene glycol having an average molecular weight of 1000 and 222 parts of isophorone diisocyanate, and a reaction was performed at 80 - 90°C for 4 h while N_2 gas was introduced.

[0102] Subsequently, 200 parts of acetone was added to make a solution, and a liquid mixture of isopropanol (100 parts) and ethylenediamine (18 parts) was added, followed by stirring at 30°C for 10 min, addition of hydrazine hydrate (20 parts) and stirring at 30°C for 1 h.

[0103] A stirred mixture of water (1360 parts) and polyoxyethylene nonyl phenol ether (150 parts: ethylene oxide added in 25 moles) was added to make a water-based system; thereafter, acetone was distilled off to yield dispersion sample No. 1 of a water-based polyurethane resin.

Comparative Synthesis Example 1

[0104] Equipment of the same construction as used in Example 1 was charged with 300 parts of polypropylene glycol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 4 h; subsequently, 24.1 parts of dimethylolpropionic acid was fed and the reaction was continued at 100 - 110°C for 2 h.

[0105] After confirming the completion of the reaction of dimethylolpropionic acid, 1130 parts of water and 16 parts of triethylamine were fed to make a water-based system; further, 14.7 parts of monoethanolamine was fed to terminate the reaction, whereby solution sample No. 11 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 21.9, neutralization rate: 100%)

Comparative Synthesis Example 2

[0106] Equipment of the same construction as used in Example 1 was charged with 300 parts of polybutylene glycol adipate diol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 4 h; subsequently, 24.1 parts of dimethylolpropionic acid was fed and the reaction was continued at 100 - 110°C for 2 h.

[0107] After confirming the completion of the reaction of dimethylolpropionic acid, 1130 parts of water and 16 parts of triethylamine were fed to make a water-based system; further, 14.7 parts of monoethanolamine was fed to terminate the reaction, whereby solution sample No. 12 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 21.9, neutralization rate: 100%)

Comparative Synthesis Example 3

[0108] Equipment of the same construction as used in Synthesis Example 1 was charged with 300 parts of a polycarbonate diol having an average molecular weight of 1000 and 133.2 parts of isophorone diisocyanate, and a reaction was performed at 100 - 105°C for 4 h while N_2 gas was introduced. Subsequently, 52.3 parts of dimethylolpropionic acid was fed and the reaction was continued at 100 - 110°C for 2h.

[0109] After confirming the completion of the reaction of dimethylolpropionic acid, 1130 parts of water and 16 parts of triethylamine were fed to make a water-based system; further, 14.7 parts of monoethanolamine was fed to terminate the reaction, whereby solution sample No. 13 of a water-based polyurethane resin was yielded. (acid value of this polyurethane resin: 21.9, neutralization rate: 100%)

Production of Water-Based Printing Ink Compositions Used for Producing Laminates and Water-Based Laminating Adhesives

[0110] In accordance with the formulae listed in Table 1, solution sample Nos. 1 - 7 and 11 - 13 of water-based polyurethane resin as prepared in Synthesis Examples 1 - 7 and Comparative Synthesis Examples 1 - 3, respectively, were mixed with a pigment under agitation for 30 min in a Red Devil type disperser; other predetermined materials were added to prepare laminating water-based printing ink samples identified as Nos. 1 - 7, 9 - 12 and five comparative samples (Comp. Nos. 1 - 5). Laminating water-based printing ink sample No. 8 was prepared as follows: 14 parts of a pigment, 1 part of a pigment dispersant BYK-181 (BYK Corp.) and 50 parts of dispersion sample No. 1 of the water-based polyurethane resin were stirred in a Red Devil type disperser and 35 parts of water was further added.

[0111] The pigment used was Fastgen Blue 5212SD (Dainippon Ink & Chemicals, Inc.), and the epoxy resin was diglycerin diglycidyl ether (Nagase Kasei Co., Ltd.; epoxy equivalent, 155).

[0112] In a separate run, solution sample Nos. 2 and 8 - 13 of water-based polyurethane resin as prepared in Synthesis Examples 2 and 8 - 10 and Comparative Synthesis Examples 1 - 3 were mixed with epoxy resin A or B under agitation in accordance with the formulae shown in Table 4, whereby water-based laminating adhesive samples identified under Nos. 1 - 8 and comparative samples identified under Comp. Nos. 1 - 5 were prepared.

[0113] Epoxy resin A was bisphenol A diglycidyl ether (Yuka Shell Epoxy Co. Ltd.; epoxy equivalent, 190), and epoxy resin B was triglycidyl trimethylolpropane (Sakamoto Yakuhin Industry Co., Ltd.; epoxy equivalent, 101).

Evaluation of Water-Based Printing Ink Sample Nos. 1 - 12 Used for Producing Laminates and Comp. Nos. 1 - 5 and Water-Based Laminating Adhesive Sample Nos. 1 - 8 and Comp. Nos. 1 - 5

[0114] Water-based printing ink sample Nos. 1 - 12 and Comp. Nos. 1 - 5 were evaluated for adhesive strength, the peel strength of extrusion laminate, the peel strength of adhesive laminate, as well as adaptabilities for boiling and retorting, and the results are shown in Tables 2 and 3.

[0115] Water-based laminating adhesive sample Nos. 1 - 8 and Comp. Nos. 1 - 5 were evaluated for the peel strength of extrusion laminate, the peel strength of adhesive laminate, as well as adaptabilities for boiling and retorting. The results are shown in Table 5.

[0116] The methods of evaluation and the criteria for evaluation were as follows, in which "OPP" means oriented polypropylene (Toyobo Co., Ltd.; P-2161, 30 μm), "PET" polyethylene terephthalate (Toyobo Co., Ltd.; E-5102, 12 μm), "NY" nylon (Unitika Ltd.; Emblem, 15 μm), and "CPP" casted polypropylene (Toray Industries, Ltd.; 60 μm).

[0117] The primer coat used in testing the peel strength of extrusion laminate on water-based printing ink sample Nos. 1 - 12 and Comp. Nos. 1 - 5 were an imine-based primer coat (Toyo Morton Co., Ltd.; EL-420) and an isocyanate base primer coat (Toyo Morton; EL-433A/C). The adhesives used in testing the peel strength of adhesive laminates on the same samples were water-based laminating adhesive sample No. 7 and an organic solvent-base isocyanate base adhesive (Takeda Chemical Industries, Ltd.; Takenate A-385/Takerak A-50).

[0118] The same films were used in the evaluations of both water-based printing inks and water-based laminating adhesives.

Adhesive Strength

[0119]

Test method: Water-based printing ink sample Nos. 1 - 12 and Comp. Nos. 1 - 5 were printed on corona-discharged OPP films in a proof press; adhesive tape was applied over the printed surface and quickly pulled off; the adhesive strength of ink was evaluated in terms of the amount of peel of the printed layer from the OPP film.

Criteria : A, No part of the printed layer was pulled off the film; B, Less than 20% in area of the printed layer was pulled off the film; C, At least 20% in area of the printed layer pulled off the film; D, From 20% to less than 50% in area of the printed layer was pulled off the film; D, At least 50% in area of the printed layer was pulled off the film.

Peel strength of extrusion laminate

[0120]

Test method: Water-based printing ink sample Nos. 1 - 12 and Comp. Nos. 1 - 5 were printed on OPP films in a proof press and, thereafter, an imine base primer coat was applied and overlaid with molten polyethylene on an extrusion laminating machine, thereby preparing laminates. In a separate run, water-based printing ink sample Nos. 1, 2, 4 - 7 and 9 - 12, as well as Comp. Nos. 2 - 5 were printed on PET or NY films in a proof press and, thereafter, an isocyanate base primer coat was applied and overlaid with molten polyethylene on an extrusion laminating machine, thereby preparing laminates. In still another run, water-based printing ink sample No. 10 was printed on OPP, PET or NY films; thereafter, water-based laminating adhesive sample Nos. 1 - 8 were applied and overlaid with molten polyethylene on an extrusion laminating machine, thereby preparing laminates.

These laminates were left to stand at 40°C for 3 days, cut to 15-mm widths and measured for T-type peel strength on a peel tester of Yasuda Seiki K.K.

Method of evaluation: Measured values of peel strength (g/15 mm) were noted.

Peel strength of adhesive laminate

[0121]

Test method: In the test on water-based printing inks, water-based laminating adhesive sample No. 7 and an organic solvent-based isocyanate base adhesive were applied to the same printed matter as used in the test for the peel strength of extrusion laminates, and the adhesive layers were overlaid with CPP film on an adhesive laminating machine, thereby preparing laminates. In the test on water-based laminating adhesives, water-based laminating adhesive sample Nos. 1 - 8 and Comp. Nos. 1 - 5 were applied to the sample printed matter as used in the test for the peel strength of extrusion laminates, and the adhesive layers were overlaid with CPP film on an adhesive laminating machine, thereby preparing laminates.

These laminates were left to stand at 40°C for 3 days, cut to 15-mm width and measured for T-type peel strength on a peel tester of Yasuda Seiki K.K.

Method of evaluation: In the test on water-based printing inks, the measured values of peel strength (g/15 mm) on the laminates coated with water-based laminating adhesive sample No. 7 were noted as "peel strength of adhesive laminate (1)", and the measured values of peel strength (g/15 mm) on the laminates coated with the organic solvent-base isocyanate base adhesive were noted as "peel strength of adhesive laminate (2)". In the test on water-based laminating adhesives, the measured values of peel strength (g/15 mm) were noted.

Adaptabilities for boiling and retorting

[0122]

Test method: In the test on water-based printing inks, the adhesive laminates made from the PET films printed with water-based printing ink sample Nos. 9 - 12 and Comp. Nos. 4 and 5 were formed into bags; in the test on water-based laminating adhesives, the adhesive laminates made from the PET films printed with water-based laminating adhesive sample Nos. 5 - 8, as well as the adhesive laminates made from the PET films printed with water-based laminating adhesive sample Nos. 5 - 8 and Comp. Nos. 4 and 5 were formed into bags; the bags thus formed were filled with a mixture of water and oil, sealed and heated in hot water at 90°C for 30 min to evaluate the adaptability for boiling; or the bags were heated in pressurized hot water at 120°C for 30 min to evaluate the adaptability for retorting. The results were rated in view of the appearance of laminates (i.e., the presence or absence of delamination).

Criteria : In the test on water-based printing inks, the adaptabilities for boiling and retorting of the laminates

coated with water-based laminating adhesive sample No. 7 were noted as "Adaptability for boiling (1)" and "Adaptability for retorting (1)", respectively, whereas the adaptabilities for boiling and retorting of the laminates coated with the organic solvent-base isocyanate-base adhesive were noted as "Adaptability for boiling (2)" and "Adaptability for retorting (2)", respectively. In the test on water-based laminating adhesives, the adaptability for boiling of the extrusion laminates, as well as the adaptabilities for boiling and retorting of the dry laminates were evaluated in view of appearance by the following criteria: A, No delaminating occurred; B, Delamination occurred as pinholes; C, Delamination occurred all over the surface.

Table 1

Formulae of Water-Based Printing Inks

	Ink No.	1	2	3	4	5	6	7	9	10	11	12
	Water-Based polyurethane resin No.	1	2	3	4	5	6	7	1	2	5	7
Ink formula (wt%)	Water-based polyurethane resin solution	50	50	50	50	50	50	50	50	50	50	50
	Pigment	14	14	14	14	14	14	14	14	14	14	14
	Isopropanol	2	2	2	2	2	2	2	2	2	2	2
	Epoxy resin	-	-	-	-	-	-	-	2	2	2	2
	Water	34	34	34	34	34	34	34	32	32	32	32

Table 1 (cont.)

Formulae of Water-Based Printing Inks

Ink No.		Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5
Water-Based polyurethane resin No.		11	12	13	12	13
Ink formula (wt%)	Water-based polyurethane resin solution	50	50	50	50	50
	Pigment	14	14	14	14	14
	Isopropanol	2	2	2	2	2
	Epoxy resin	-	-	-	2	2
	Water	34	34	34	32	32

Table 2

Results of Evaluation of Water-Based Printing Inks and Laminates											
Ink No.		1	2	3	4	5	6	7	Comp. 1	Comp. 2	Comp. 3
Adhesive Strength *)		A	A	A	A	A	A	A	D	D	B
Peel strength of extrusion laminate *)	OPP	210	220	150	190	200	100	210	5	15	30
	PET	500	500	-	500	500	500	500	-	150	290
	NY	500	500	-	500	500	500	500	-	190	300
Peel strength of adhesive laminate (1)	OPP	190	200	220	190	200	200	210	20	50	150
	PET	500	250	-	310	500	300	370	-	250	250
	NY	500	300	-	360	500	420	500	-	260	310
Peel strength of adhesive laminate (2)*)	OPP	190	200	200	220	210	200	180	20	50	100
	PET	500	300	-	270	500	330	500	-	240	300
	NY	500	440	-	400	500	360	500	-	300	300

*) (for comparison)

Table 3

Results of Evaluation of Water-Based Printing Inks and Laminates							
Ink No.		9	10	11	12	Comp. 4	Comp. 5
Adhesive strength*)		A	A	A	A	D	B
Peel strength of extrusion laminate *)	OPP	210	240	200	220	15	30
	PET	500	500	500	500	150	210
	NY	500	500	500	500	260	300
Peel strength of adhesive laminate (1)	OPP	190	190	210	220	50	140
	PET	500	320	430	500	250	290
	NY	500	500	500	500	80	330
Peel strength of adhesive laminate (2)*)	OPP	200	210	220	220	50	160
	PET	500	310	500	500	300	300
	NY	500	500	500	500	310	340
Adaptability for boiling (1)	PET	A	A	A	A	C	B
Adaptability for boiling (2) *)	PET	A	A	A	A	C	B
Adaptability for retorting (1)	PET	A	A	A	A	C	B
Adaptability for retorting (2) *)	PET	A	A	A	A	C	B

*) (for comparison)

Table 4

Formulae of Water-Based Laminating Adhesives

Adhesive No.		1*)	2*)	3*)	4*)	5	6	7	8
Water-Based polyurethane resin solution No.		2	8	9	10	2	2	2	2
Adhesive formula (wt%)	Content of water-based polyurethane resin solution	100	100	100	100	93	93	89	77
	Content of epoxy resin A	-	-	-	-	7	-	-	-
	Content of epoxy resin B	-	-	-	-	-	7	11	23
Polyurethane resin/epoxy resin weight ratio as ratio as solids content		80/20	80/20	70/30	70/30	80/20	80/20	70/30	50/50

*) (for comparison)

Table 4 (cont.)

Formulae of Water-Based Laminating Adhesives

Adhesive No.		Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5
Water-Based polyurethane resin solution No.		11	12	13	12	13
Adhesive formula (wt%)	Content of water-based polyurethane resin solution	100	100	100	89	89
	Content of epoxy resin A	-	-	-	-	-
	Content of epoxy resin B	-	-	-	11	11
Polyurethane resin/epoxy resin weight ratio as ratio as solids content		100/0	100/0	100/0	70/30	70/30

Table 5

Results of Evaluation of Water-Based Laminating Adhesives

Adhesive No.			1*)	2*)	3*)	4*)	5	6	7	8
Extrusion laminate	Peel strength of laminate	OPP	190	200	210	190	220	230	200	200
		PET	450	500	480	490	500	500	520	480
		NY	500	500	500	500	500	500	500	500
	Adaptability for boiling		-	-	-	-	B	B	A	A
Adhesive laminate	Peel strength of laminate	OPP	150	210	240	220	200	170	190	210
		PET	460	500	500	460	500	480	320	500
		NY	500	500	500	500	500	460	500	500
	Adaptability for boiling		-	-	-	-	A	A	A	A
	Adaptability for retorting		-	-	-	-	B	B	A	A

*) (for comparison)

Table 5 (cont.)

Results of Evaluation of Water-Based Laminating Adhesives

Adhesive No.			Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5
Extrusion laminate	Peel strength of laminate	OPP	-	-	-	-	-
		PET	-	-	-	-	-
		NY	-	-	-	-	-
	Adaptability for boiling		-	-	-	-	-
Adhesive laminate	Peel strength of laminate	OPP	30	50	50	50	70
		PET	50	100	140	90	100
		NY	150	90	100	100	100
	Adaptability for boiling		-	-	-	C	C
	Adaptability for retorting		-	-	-	C	C

[0123] As described above specifically with reference to working examples, the water-based polyurethane resin specified in the present invention can be used as water-based laminating adhesives. The water-based printing ink compositions that use this water-based polyurethane resin exhibit satisfactory adhesion to various kinds of plastic films. The laminaies produced by the combined use of that ink composition with the water-based laminating adhesive are totally water-based and exhibit high strength; at the same time, they have good adaptabilities for boiling and retorting.

Claims

1. A water-based laminating adhesive containing a water-based polyurethane resin and a water-soluble or a water-reducible epoxy resin,

said water-based polyurethane resin having a number average molecular weight of 2,000 - 200,000 and being

prepared by reacting an organic diisocyanate compound, a polymer diol compound, a chain extender and a terminator, wherein a chain extender and/or a terminator that has at least one hydrazine group or hydrazide group is used to incorporate at least one group selected from hydrazine groups, hydrazide groups, and semicarbazide groups in the molecule of the polyurethane resin;
wherein said organic diisocyanate compound being selected from the group consisting of aliphatic diisocyanate compounds; alicyclic diisocyanate compounds; aroaliphatic diisocyanate compounds; and aromatic diisocyanate compounds;

said polymer diol compound being selected from the group consisting of polyester diols that are prepared by polycondensation of low-molecular weight diols with dibasic acid compounds or by the ring opening reaction of cyclic ester compounds; polyether diols that are prepared by homo- or copolymerizing ethylene oxide, propylene oxide or tetrahydrofuran; polycarbonate diols that are prepared by reacting carbonate compounds or phosgene with said low-molecular weight diol components; and polybutadiene glycols;
said chain extender being selected from the group consisting of polyamino hydrazine compounds that are represented by the following general formula (2):

$$H_2N - R_1 - NH - CH_2 - \underset{\displaystyle R_2}{\underset{|}{CH}} - \underset{\displaystyle O}{\underset{\|}{C}} - NH - NH_2 \qquad \cdots (2)$$

where R_1 is an alkylene group having 2 to 15 carbon atoms, that portion of an alicyclic or aromatic diamine having 6 to 15 carbon atoms which excludes the amino group or that portion of a polyethylene polyamine having 3 to 5 nitrogen atoms which excludes the primary amino group, and R_2 is hydrogen or a methyl group; compounds having a tertiary amino group; carboxylic acid compounds represented by the following general formula (3):

$$HO - CH_2 - \underset{\displaystyle COOH}{\underset{|}{\overset{\displaystyle R_3}{\overset{|}{C}}}} - CH_2 - OH \qquad \cdots (3)$$

where R_3 is a hydrogen atom or a straight-chained or branched alkyl group having 1 to 8 carbon atoms; diols containing an aliphatic carboxylic acid group and being formed by reacting succinic anhydride or maleic anhydride with lower triols; diols containing aromatic carboxylic acid groups and being formed by reacting phthalic anhydride or trimellitic anhydride with lower triols or pyromellitic anhydride with lower diols; glycols; aliphatic diamines; aliphatic polyols; alicyclic polyols; and aliphatic polyamines; and
said terminator being selected from the group consisting of the compounds listed above as chain extenders, hydrazine, alkylene dihydrazines, alkylene dihydrazides, and dihydrazide compounds of saturated aliphatic dibasic acids or unsaturated dibasic acids that are represented by the following general formula (4):

$$H_2N - NH - X - NH - NH_2 \qquad (4)$$

where X is an alkylene group having 1 to 8 carbon atoms or a carbonyl residue of a saturated or unsaturated dibasic acid having 1 to 10 carbon atoms; alkyl amines; alkanol amines; and monoalcohols; and
the weight ratio of the solids content of said water-based polyurethane resin to that of the epoxy resin being from 99:1 to 50:50.

2. A process for producing a laminate that comprises printing a water-based ink composition for printing on a plastic film, then applying the adhesive of claim 1 to the printing surface, and thereafter laminating a molten polymer or polymer film thereon, wherein said ink composition comprises a pigment, water and a binder resin,

said binder resin being a water-based polyurethane resin having a number average molecular weight of 2,000 - 200,000 that is prepared by reacting an organic diisocyanate compound, a polymer diol compound, a chain extender and a terminator, wherein a chain extender and/or a terminator that has at least one hydrazine group

or hydrazide group is used to incorporate at least one group selected from hydrazine groups, hydrazide groups, and semicarbazide groups in the molecule of the polyurethane resin;
wherein said organic diisocyanate compound being selected from the group consisting of aliphatic diisocyanate compounds; alicyclic diisocyanate compounds; aroaliphatic diisocyanate compounds; and aromatic diisocyanate compounds;
said polymer diol compound being selected from the group consisting of polyester diols that are prepared by polycondensation of low-molecular weight diols with dibasic acid compounds or by the ring opening reaction of cyclic ester compounds; polyether diols that are prepared by homo- or copolymerizing ethylene oxide, propylene oxide or tetrahydrofuran; polycarbonate diols that are prepared by reacting carbonate compounds or phosgene with said low-molecular weight diol components; and polybutadiene glycols;
said chain extender being selected from the group consisting of polyamino hydrazine compounds that are represented by the following general formula (2):

$$H_2N - R_1 - NH - CH_2 - \underset{\displaystyle R_2}{\underset{|}{CH}} - \underset{\displaystyle O}{\underset{\|}{C}} - NH - NH_2 \quad \cdots \quad (2)$$

where R_1 is an alkylene group having 2 to 15 carbon atoms, that portion of an alicyclic or aromatic diamine having 6 to 15 carbon atoms which excludes the amino group or that portion of a polyethylene polyamine having 3 to 5 nitrogen atoms which excludes the primary amino group, and R_2 is hydrogen or a methyl group; compounds having a tertiary amino group; carboxylic acid compounds represented by the following general formula (3):

$$HO - CH_2 - \overset{\displaystyle R_3}{\overset{|}{\underset{\displaystyle COOH}{\underset{|}{C}}}} - CH_2 - OH \quad \cdots \quad (3)$$

where R_3 is a hydrogen atom or a straight-chained or branched alkyl group having 1 to 8 carbon atoms; diols containing an aliphatic carboxylic acid group and being formed by reacting succinic anhydride or maleic anhydride with lower triols; diols containing aromatic carboxylic acid groups and being formed by reacting phthalic anhydride or trimellitic anhydride with lower triols or pyromellitic anhydride with lower diols; glycols; aliphatic diamines; aliphatic polyols; alicyclic polyols; and aliphatic polyamines; and
said terminator being selected from the group consisting of the compounds listed above as chain extenders, hydrazine, alkylene dihydrazines, alkylene dihydrazides, and dihydrazide compounds of saturated aliphatic dibasic acids or unsaturated dibasic acids that are represented by the following general formula (4):

$$H_2N - NH - X - NH - NH_2 \qquad (4)$$

where X is an alkylene group having 1 to 8 carbon atoms or a carbonyl residue of a saturated or unsaturated dibasic acid having 1 to 10 carbon atoms; alkyl amines; alkanol amines; and monoalcohols.

3. The process according to claim 2, in which said water-based polyurethane resin contained in the ink composition is one prepared by dispersing the polyurethane resin in water in an amount of 5 - 50 wt% as solids content in the presence of an emulsifier.

4. The process according to claim 2, in which said water-based polyurethane resin contained in the ink composition is one prepared by dissolving or dispersing the polyurethane resin having an acid value of 5 - 100 in an aqueous solution in the presence of alkali in an amount being 0.15 - 1.2 times the equivalent amount necessary to achieve neutralization.

5. The process according to claim 2, in which said water-based polyurethane resin contained in the ink composition

is one prepared by dissolving or dispersing the polyurethane resin having an amino value of 10 - 40 in an aqueous solution in the presence of acid in an amount being 0.15 - 1.2 times the equivalent amount necessary to achieve neutralization.

6. A process according to any of claims 2 to 5, wherein the ink composition further contains a water-soluble or a water-reducible epoxy resin, the weight ratio of the solids content of said water-based polyurethane resin to that of the epoxy resin being from 99:1 to 50:50.

Patentansprüche

1. Laminierklebstoff auf wässeriger Basis, der ein Polyurethanharz auf wässeriger Basis und ein wasserlösliches oder wassermischbares Epoxyharz enthält,

wobei das Polyurethanharz auf wässeriger Basis ein Zahlenmittel des Molekulargewichts von 2000 bis 200 000 hat und durch Umsetzen einer organischen Diisocyanatverbindung, einer Polymerdiolverbindung, eines Kettenverlängerers und eines Terminators hergestellt ist, wobei ein Kettenverlängerer und/oder bin Terminator, der mindestens eine Hydrazingruppe oder eine Hydrazidgruppe hat, eingesetzt wird, um mindestens eine unter Hydrazingruppen, Hydrazidgruppen und Semicarbazidgruppen ausgewählte Gruppe in das Molekül des Polyurethanharzes einzubauen;
wobei die organische Diisocyanatverbindung aus der Gruppe ausgewählt ist, die aus aliphatischen Diisocyanatverbindungen, alicyclischen Diisocyanatverbindungen, araliphatischen Diisocyanatverbindungen und aromatischen Diisocyanatverbindungen besteht;
die Polymerdiolverbindung auf der Gruppe ausgewählt ist, die aus Polyesterdiolen, die durch Polykondensation von niedermolekularen Diolen mit dibasischen Säureverbindungen oder durch die Ringöffnungsreaktion von cyclischen Esterverbindungen hergestellt sind, Polyetherdiolen, die durch Homopolymerisation oder Copolymerisation von Ethylenoxid, Propylenoxid oder Tetrahydrofuran hergestellt sind, Polycarbonatdiolen, die durch Umsetzen von Carbonatverbindungen oder Phosgen mit den niedermolekularen Diolkomponenten hergestellt sind, und Polybutadienglycolen besteht,
der Kettenverlängerer aus der Gruppe ausgewählt ist, die aus Polyaminohydrazinverbindungen, die durch die folgende allgemeine Formel (2) dargestellt wird:

$$H_2N - R_1 - NH - CH_2 - \underset{\displaystyle R_2}{\underset{|}{CH}} - \underset{\displaystyle O}{\underset{\|}{C}} - NH - NH_2 \quad \cdots (2)$$

worin R_1 eine Alkylengruppe mit 2 bis 15 Kohlenstoffatomen, der Teil eines alicyclischen oder aromatischen Diamins mit 6 bis 15 Kohlenstoffatomen, der die Aminogruppe ausschließt, oder der Teil eines Polyethylenpolyamins mit 3 bis 5 Stickstoffatomen ist, der die primäre Aminogruppe ausschließt, und R_2 Wasserstoff oder eine Methylgruppe ist;
Verbindungen mit einer tertiären Aminogruppe; Carbonsäureverbindungen, die durch die folgende allgemeine Formel (3) dargestellt werden:

$$HO - CH_2 - \overset{\displaystyle R_3}{\overset{|}{\underset{\displaystyle COOH}{\underset{|}{C}}}} - CH_2 - OH \quad \cdots (3)$$

worin R_3 ein Wasserstoffatom oder eine geradkettige oder verzweigte Alkylgruppe mit 1 bis 8 Kohlenstoffatomen ist;
Diolen, die eine aliphatische Carbonsäuregruppe enthalten und durch Umsetzen von Bernsteinsäureanhydrid oder Maleinsäureanhydrid mit niederen Triolen gebildet sind; Diolen, die aromatische Carbonsäuregruppen enthalten und durch Umsetzen von Phthalsäureanhydrid oder Trimellithsäureanhydrid mit niederen Triolen

oder Pyromellithsäureanhydrid mit niederen Diolen gebildet sind; Glycolen; aliphatischen Diaminen; aliphatischen Polyolen; alicyclischen Polyolen; und aliphatischen Polyaminen besteht; und

der Terminator aus der Gruppe ausgewählt ist, die aus den vorstehend als Kettenverlängerer aufgelisteten Verbindungen, Hydrazin, Alkylendihydrazinen, Alkylendihydraziden und Dihydrazidverbindungen von gesättigten aliphatischen dibasischen Säuren oder ungesättigten dibasischen Säuren, die durch die folgende allgemeine Formel (4) dargestellt sind:

$$H_2N - NH - X - NH - NH_2 \qquad (4)$$

worin X eine Alkylengruppe mit 1 bis 8 Kohlenstoffatomen oder ein Carbonylrest einer gesättigten oder ungesättigten dibasischen Säure mit 1 bis 10 Kohlenstoffatomen ist; Alkylaminen; Alkanolaminen und Monoalkoholen besteht; und

das Gewichtsverhältnis des Feststoffgehalts Polyurethanharzes auf wässeriger Basis zu dem des Epoxyharzes 99:1 bis 50:50 ist.

2. Verfahren zur Herstellung eines Laminats, das das Drucken einer Druckfarbenzusammensetzung auf wässeriger Basis zum Drucken auf eine Plastikfolie, das anschließende Auftragen des Klebstoffs gemäß Anspruch 1 auf die Druckoberfläche und dann das Aufkaschieren eines geschmolzenen Polymers oder einer Polymerfolie umfaßt, wobei die Druckfarbenzusammensetzung ein Pigment, Wasser und ein Binderharz umfaßt,

das Binderharz ein Polyurethanharz auf wässeriger Basis mit einem Zahlenmittel des Molekulargewichts von 2000 bis 200 000 ist, das durch Umsetzen einer organischen Diisocyanatverbindung, einer Polymerdiolverbindung, eines Kettenverlängerers und eines Terminators hergestellt ist, wobei ein Kettenverlängerer und/oder ein Terminator, der mindestens eine Hydrazingruppe oder eine Hydrazidgruppe hat, eingesetzt wird, um mindestens eine unter Hydrazingruppen, Hydrazidgruppen und Semicarbazidgruppen ausgewählte Gruppe in das Molekül des Polyurethanharzes einzubauen;

die organische Diisocyanatverbindung aus der Gruppe ausgewählt ist, die aus aliphatischen Diisocyanatverbindungen, alicyclischen Diisocyanatverbindungen, araliphatischen Diisocyanatverbindungen und aromatischen Diisocyanatverbindungen besteht;

die Polymerdiolverbindung aus der Gruppe ausgewählt ist, die aus Polyesterdiolen, die durch Polykondensation von niedermolekularen Diolen mit dibasischen Säureverbindungen oder durch die Ringöffnungsreaktion von cyclischen Esterverbindungen hergestellt sind; Polyetherdiolen, die durch Homopolymerisation oder Copolymerisation von Ethylenoxid, Propylenoxid oder Tetrahydrofuran hergestellt sind; Polycarbonatdiolen, die durch Umsetzen von Carbonatverbindungen oder Phosgen mit den niedermolekularen Diolkomponenten hergestellt sind; und Polybutadienglycolen besteht;

der Kettenverlängerer aus der Gruppe ausgewählt ist, die aus Polyaminohydrazinverbindungen, die durch die folgende allgemeine Formel (2) dargestellt werden:

$$H_2N - R_1 - NH - CH_2 - \underset{\displaystyle R_2}{\underset{|}{CH}} - \underset{\displaystyle O}{\underset{\|}{C}} - NH - NH_2 \quad \cdots \quad (2)$$

worin R_1 eine Alkylengruppe mit 2 bis 15 Kohlenstoffatomen, der Teil eines alicyclischen oder aromatischen Diamins mit 6 bis 15 Kohlenstoffatomen, der die Aminogruppe ausschließt, oder der Teil eines Polyethylenpolyamins mit 3 bis 5 Stickstoffatomen ist, der die primäre Aminogruppe ausschließt, und R_2 Wasserstoff oder eine Methylgruppe ist;

Verbindungen mit einer tertiären Aminogruppe; Carbonsäureverbindungen, die durch die folgende allgemeine Formel (3) dargestellt sind:

$$\begin{array}{c} \quad\quad\quad\quad\quad\quad R_3 \\ \quad\quad\quad\quad\quad\quad | \\ HO - CH_2 - C - CH_2 - OH \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad COOH \end{array} \quad \cdots (3)$$

worin R_3 ein Wasserstoffatom oder eine geradkettige oder verzweigte Alkylgruppe mit 1 bis 8 Kohlenstoffatomen ist;

Diolen, die eine aliphatische Carbonsäuregruppe enthalten und durch Umsetzen von Bernsteinsäureanhydrid oder Maleinsäureanhydrid mit niederen Triolen gebildet sind; Diolen, die aromatische Carbonsäuregruppen enthalten und durch Umsetzen von Phthalsäureanyhdrid oder Trimellithsäureanhydrid mit niederen Triolen oder Pyromellithsäureanhydrid mit niederen Diolen gebildet sind; Glycolen; aliphatischen Diaminen; aliphatischen Polyolen; alicyclischen Polyolen; und aliphatischen Polyaminen besteht; und

der Terminator aus der Gruppe ausgewählt ist, die aus den vorstehend als Kettenverlängerer aufgelisteten Verbindungen, Hydrazin, Alkylendihydrazinen, Alkylendihydraziden und Dihydrazidverbindungen von gesättigten aliphatischen dibasischen Säuren oder ungesättigten dibasischen Säuren, die durch die folgende allgemeine Formel (4) dargestellt werden:

$$H_2N - NH - X - NH - NH_2 \quad (4)$$

worin X eine Alkylengruppe mit 1 bis 8 Kohlenstoffatomen oder ein Carbonylrest einer gesättigten oder ungesättigten dibasischen Säure mit 1 bis 10 Kohlenstoffatomen ist; Alkylaminen, Alkanolaminen und Monoalkoholen besteht.

3. Verfahren gemäß Anspruch 2, wobei das Polyurethanharz auf wässeriger Basis, das in der Druckfarbenzusammensetzung enthalten ist, eines ist, das durch Dispergieren des Polyurethanharzes in einer Menge von 5 bis 50 Gew.-% als Feststoffgehalt in Wasser in Anwesenheit eines Emulgiermittels hergestellt ist.

4. Verfahren gemäß Anspruch 2, wobei das Polyurethanharz auf wässeriger Basis, das in der Druckfarbenzusammensetzung enthalten ist, eines ist, das durch Auflösen oder Dispergieren des Polyurethanharzes mit einer Säurezahl von 5 bis 100 in einer wäßrigen Lösung in Anwesenheit einer Base in einer Menge, die das 0,15 bis 1,2-fache der für das Erreichen der Neutralisation erforderlichen Äquivalentmenge ist, hergestellt ist.

5. Verfahren gemäß Anspruch 2, wobei das Polyurethanharz auf wässeriger Basis, das in der Druckfarbenzusammensetzung enthalten ist, eines ist, das durch Auflösen oder Dispergieren des Polyurethanharzes mit einer Säurezahl von 10 bis 40 in einer wäßrigen Lösung in Anwesenheit einer Säure in einer Menge, die das 0,15 bis 1,2-fache der für das Erreichen der Neutralisation erforderlichen Äquivalentmenge ist, hergestellt ist.

6. Verfahren gemäß einem der Ansprüche 2 bis 5, wobei die Druckfarbenzusammensetzung zusätzlich ein wasserlösliches oder ein wassermischbares Epoxyharz enthält, wobei das Gewichtsverhältnis des Feststoffgehalts des Polyurethanharzes auf wässeriger Basis zu dem des Epoxyharzes 99:1 bis 50:50 ist.

Revendications

1. Adhésif de stratification à base aqueuse contenant une résine polyuréthanne à base aqueuse et une résine époxy soluble dans l'eau ou diluable par l'eau,

ladite résine polyuréthanne à base aqueuse ayant un poids moléculaire moyen en nombre de 2000 à 200 000 et étant préparée en faisant réagir un diisocyanate organique, un polymère-diol, un agent d'allongement de chaîne et un agent de terminaison où un agent d'allongement de chaîne et/ou un agent de terminaison ayant au moins un groupe hydrazine ou un groupe hydrazide est/sont utilisé(s) pour incorporer au moins un groupe choisi parmi les groupes hydrazine, les groupes hydrazide et les groupes semicarbazide dans la molécule de la résine polyuréthanne ;

ledit diisocyanate organique étant choisi dans la classe formée par les diisocyanates aliphatiques, les diisocyanates alicycliques, les diisocyanates aromatiques-aliphatiques et les diisocyanates aromatiques ;

ledit polymère-diol étant choisi dans la classe formée par les polyester-diols qui sont préparés par polycondensation de diols de bas poids moléculaire avec des diacides ou par la réaction d'ouverture de cycle d'esters cycliques ; les polyéther-diols qui sont préparés par homo-ou copolymérisation d'oxyde d'éthylène, d'oxyde de propylène ou de tétrahydrofuranne ; les polycarbonate-diols qui sont préparés par la réaction de carbonates ou du phosgène avec lesdits composants diols de bas poids moléculaire ; et les polybutadiène-glycols ;

ledit agent d'allongement de chaîne étant choisi dans la classe formée par les polyamino-hydrazines qui sont représentées par la formule générale (2) suivante :

$$H_2N-R_1-NH-CH_2-\underset{R_2}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-NH-NH_2 \qquad \ldots (2)$$

où R_1 est un groupe alkylène ayant 2 à 15 atomes de carbone, la portion d'une diamine alicyclique ou aromatique ayant 6 à 15 atomes de carbone qui exclut le groupe amino ou la portion d'une polyéthylène-polyamine ayant 3 à 5 atomes d'azote qui exclut le groupe amino primaire, et R_2 est un atome d'hydrogène ou un groupe méthyle ; les composés ayant un groupe amino tertiaire ; les acides carboxyliques représentés par la formule générale (3) suivante :

$$HO-CH_2-\overset{R_3}{\underset{COOH}{\overset{|}{\underset{|}{C}}}}-CH_2-OH \qquad \ldots (3)$$

où R_3 est un atome d'hydrogène ou un groupe alkyle à chaîne droite ou ramifiée ayant 1 à 8 atomes de carbone ; les diols contenant un groupe acide carboxylique aliphatique et formés en faisant réagir l'anhydride succinique ou l'anhydride maléique avec des triols inférieurs ; les diols contenant des groupes acide carboxylique aromatique et formés en faisant réagir l'anhydride phtalique ou l'anhydride trimellique avec des triols inférieurs ou l'anhydride pyromellique avec des diols inférieurs ; les glycols ; les diamines aliphatiques ; les polyols aliphatiques ; les polyols alicycliques ; et les polyamines aliphatiques ; et

ledit agent de terminaison étant choisi dans la classe formée par les composés énoncés ci-dessus comme agents d'allongement de chaîne, l'hydrazine, les alkylène-dihydrazines, les alkylène-dihydrazides, et les dihydrazides de diacides aliphatiques saturés ou de diacides insaturés qui sont représentés par la formule générale (4) suivante :

$$H_2N\text{-}NH\text{-}X\text{-}NH\text{-}NH_2 \qquad (4)$$

où X est un groupe alkylène ayant 1 à 8 atomes de carbone ou un résidu carbonylé d'un diacide saturé ou insaturé ayant 1 à 10 atomes de carbone ; les alkylamines ; les alcanol-amines ; et les monoalcools ; et

le rapport en poids de la teneur en matière sèche de ladite résine polyuréthanne à base aqueuse à celle de la résine époxy étant de 99:1 à 50:50.

2. Procédé de production d'un stratifié qui comprend l'impression d'une feuille de matière plastique avec une composition d'encre à base aqueuse pour impression, puis l'application de l'adhésif de la revendication 1 à la surface d'impression, et ensuite la stratification sur celle-ci d'un polymère fondu ou d'une feuille de polymère, dans lequel ladite composition d'encre comprend un pigment, de l'eau et une résine liante,

ladite résine liante étant une résine polyuréthanne à base aqueuse ayant un poids moléculaire moyen en nombre de 2000 à 200 000, qui est préparée en faisant réagir un diisocyanate organique, un polymère-diol, un agent d'allongement de chaîne et un terminateur, où un agent d'allongement de chaîne et/ou un agent de terminaison ayant au moins un groupe hydrazine ou un groupe hydrazide est/sont utilisé(s) pour incorporer au moins un groupe choisi parmi les groupes hydrazine, les groupes hydrazide et les groupes semicarbazide dans la molécule de la résine polyuréthanne ;

ledit diisocyanate organique étant choisi dans la classe formée par les diisocyanates aliphatiques, les diisocyanates alicycliques, les diisocyanates aromatiques-aliphatiques et les diisocyanates aromatiques ;

ledit polymère-diol étant choisi dans la classe formée par les polyester-diols qui sont préparés par polycondensation de diols de bas poids moléculaire avec des diacides ou par la réaction d'ouverture de cycle d'esters

cycliques ; les polyéther-diols qui sont préparés par homo- ou copolymérisation d'oxyde d'éthylène, d'oxyde de propylène ou de tétrahydrofuranne ; les polycarbonate-diols qui sont préparés par la réaction de carbonates ou du phosgène avec lesdits composants diols de bas poids moléculaire ; et les polybutadiène-glycols ;
ledit agent d'allongement de chaîne étant choisi dans la classe formée par les polyamino-hydrazines qui sont représentées par la formule générale (2) suivante :

$$H_2N-R_1-NH-CH_2-\underset{\displaystyle R_2}{\underset{|}{C}H}-\underset{\displaystyle O}{\underset{\|}{C}}-NH-NH_2 \quad \ldots (2)$$

où R_1 est un groupe alkylène ayant 2 à 15 atomes de carbone, la portion d'une diamine alicyclique ou aromatique ayant 6 à 15 atomes de carbone qui exclut le groupe amino ou la portion d'une polyéthylène-polyamine ayant 3 à 5 atomes d'azote qui exclut le groupe amino primaire, et R_2 est un atome d'hydrogène ou un groupe méthyle ; les composés ayant un groupe amino tertiaire ; les acides carboxyliques représentés par la formule générale (3) suivante :

$$HO-CH_2-\overset{\displaystyle R_3}{\overset{|}{\underset{\displaystyle COOH}{\underset{|}{C}}}}-CH_2-OH \quad \ldots (3)$$

où R_3 est un atome d'hydrogène ou un groupe alkyle à chaîne droite ou ramifiée ayant 1 à 8 atomes de carbone ; les diols contenant un groupe acide carboxylique aliphatique et formés en faisant réagir l'anhydride succinique ou l'anhydride maléique avec des triols inférieurs ; les diols contenant des groupes acide carboxylique aromatique et formés en faisant réagir l'anhydride phtalique ou l'anhydride trimellique avec des triols inférieurs ou l'anhydride pyromellique avec des diols inférieurs ; les glycols ; les diamines aliphatiques ; les polyols aliphatiques ; les polyols alicycliques ; et les polyamines aliphatiques ; et
ledit agent de terminaison étant choisi dans la classe formée par les composés énoncés ci-dessus comme agents d'allongement de chaîne, l'hydrazine, les alkylène-dihydrazines, les alkylène-dihydrazides, et les dihydrazides de diacides aliphatiques saturés ou de diacides insaturés qui sont représentés par la formule générale (4) suivante :

$$H_2N\text{-}NH\text{-}X\text{-}NH\text{-}NH_2 \quad (4)$$

où X est un groupe alkylène ayant 1 à 8 atomes de carbone ou un résidu carbonylé d'un diacide saturé ou insaturé ayant 1 à 10 atomes de carbone ; les alkylamines ; les alcanol-amines ; et les monoalcools.

3. Procédé selon la revendication 2, dans lequel ladite résine polyuréthanne à base aqueuse contenue dans la composition d'encre est préparée en dispersant la résine polyuréthanne dans de l'eau en une proportion de 5 à 50 % en poids de matière sèche en présence d'un émulsifiant.

4. Procédé selon la revendication 2, dans lequel ladite résine polyuréthanne à base aqueuse contenue dans la composition d'encre est préparée en dissolvant ou dispersant la résine polyuréthanne ayant un indice d'acide de 5 à 100 dans une solution aqueuse en présence d'un alcali en une quantité de 0,15 à 1,2 fois la quantité équivalente nécessaire pour atteindre la neutralisation.

5. Procédé selon la revendication 2, dans laquelle ladite résine polyuréthanne à base aqueuse contenue dans la composition d'encre est préparée en dissolvant ou dispersant la résine polyuréthanne ayant un indice d'amine de 10 à 40 dans une solution aqueuse en présence d'un acide en une quantité de 0,15 à 1,2 fois la quantité équivalente nécessaire pour atteindre la neutralisation.

6. Procédé selon l'une quelconque des revendications 2 à 5, dans lequel la composition d'encre contient, de plus, une résine époxy soluble dans l'eau ou diluable par l'eau, le rapport en poids de la teneur en matière sèche de ladite résine polyuréthanne à base aqueuse à celle de la résine époxy étant de 99:1 à 50:50.